STUDY OF A SPECIAL CASE OF IN SITU IRON AND MANGANESE ELIMINATION: THE VYREDOX AND THE SUBTERRA METHODS (WATERWORK GESZTELY – I)

by

I. ORSOVAI

Institute of Applied and Engineering Geology, Eötvös Loránd University, Budapest

(Received: 30th March, 1988)

Abstract

Due to a technical failure in the iron-manganese elimination experiment (Vyredox method) tried in a producing well, originally surrounded by three absorbing wells, had to be transformed into a so-called subterra system of alternating function in a single well.

The same hydrogeological and operating circumstances enabled us to make a comparison between the two methods. According by, both methods are suitable for iron-manganese elimination under the hydrogeological conditions given.

Calculations for the subterra method have shown the method just economical with a pertinent water quality still acceptable when keeping a ratio of 1 to 4 between water intake and production.

Introduction

The in situ iron-manganese elimination methods act basically in two different systems:

a) The water, enriched in oxygene, is recharched in three or more test wells around the producing well.

b) On single well serves alternatively for recharge and a production as well.

The efficiency of the two methods is approximately the same; it depends on technical and economical parameters which method is more suitable in a certain case.

Though both methods are well-known and widely studied, this is their first comparative examination made in Hungary. Both methods were applied to the same well at different time.

Geological and hydrogeological make up

The study area is situated on the gravel terrace of the river Hernád, which is considered to be Early Holocene – Late Pleistocene because it lies +110 – +112 m above the sea level (Fig. 1.).

According to the generalizable sequence of the study area, from the surface the A+B+C level of the soil is approximately 1 m thick, under which brown sandy clay about 15 m thick can be found.

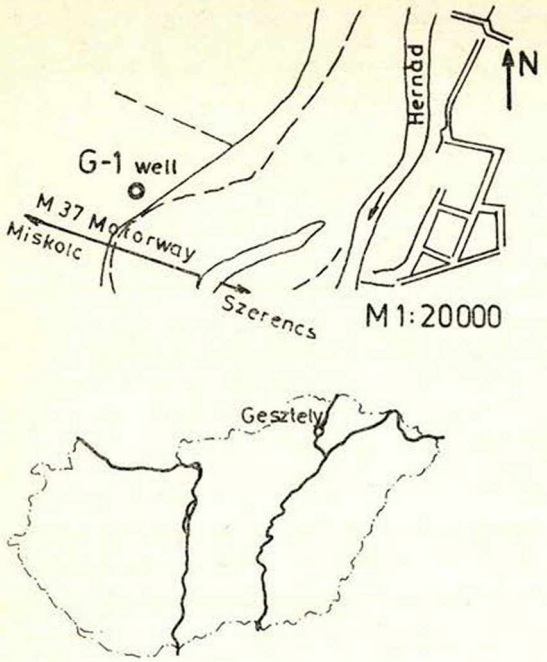

Fig. 1. Locality of experiments

The waterbearing sandy gravel sequence is about a 20 m thick, yellow, red-brown, unconsolidated, somewhat silty, medium-and-coarse grained, with *sand* composed of grains of 0,1 – 2,0 mm, moderately rounded, with no mica.

Pebbles are of quartz, quartzite, generally with brown crust (iron coating) being as large as 2 – 5 mm in diameter. Because of the silt content the rock is compact when dried up.

Lime content is small, 0,3 – 3,0% with a weighted average of 0,8%, therefore incapable to adsorb the agressive CO_2 quantity.

The upper part of the underlying bed is a 0,2 m-thick clay the upper part of which is yellow, the lower one grey.

The sequence of test well G – 1:

	Rock description
0,0 – 1,0 m	*Clay* Brown, strongly coherent, with no lime content, containing recent plant remains

1 – 1,9 m *Sand*

Yellow-grey, loose, medium calcareous (+ +), medium grained: 0,2 – 0,5 mm in diameter, it contains quartz and mafic components, devoid of mica, and moderately rounded

1,9 – 19,8 m *Gravelly sand*

Yellow-grey, unconsolidated, medium-calcareous (+ +) sequence, the *sand* is approximately half medium and half coarse grained of 0,2 – 2,0 mm in diameter; with quartz and mafic components, without mica and moderately rounded; the *gravel* is multi-coloured, consisting of quartz and quartzite, 1 – 3 cm large in diameter and moderately rounded

19,8 – 22,0 m *Sand*

Yellow-grey, unconsolidated, medium-calcareous (+ +) 0,2 – 0,5 mm in diameter, with quartz and mafic components, devoid of mica and moderately rounded

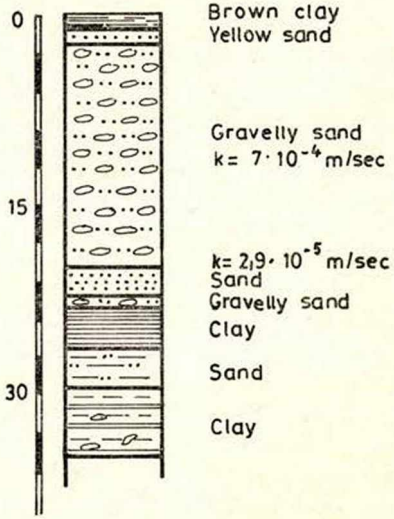

Fig. 2. Successive layers of G-1. well

22,0 – 23,0 m *Gravelly sand*

Yellow-grey, unconsolidated, medium-calcareous (+ +) approximately half of the sand is medium-grained and a half part of it coarse-grained (0,2 – 2,0 mm) with quartz and mafic components, without mica moderately rounded; the gravel (1 – 3 cm) multi-coloured, consist of quartz and quartzite, moderately rounded

23,0 – 26,0 m *Clay*

Yellow-grey, coherent medium-calcareous (+ +)

26,0 – 29,0 m *Silty – sand*

Yellow-grey, coherent, medium-calcareous (+ +), limonite-mottled, lime concretionary with high silt content (Fig. 2.)

Three drain-wells were installed at a distance of five metres around test well G – 1 at an angle of 120°. The core samples were subjected to mineralogical, petrological and chemical analyses. These examinations had two purposes: first of all we wanted to make clear the origin of the iron-manganese and to estimate the quantity of its future amount; on the other hand we wanted to examine the possible influence of the water-bearing rock on the iron-manganese elimination process.

The oldest formation examined was a material classified to belong to the lower part of the Upper Pannonian substage (Congeria ungula caprae level), it deposited under brackish water conditions. However, it can be found in situ only in the deep underlying bed. It has been observed that due to drenching the upper part of the clay became loose and local stream water erosion, removed it. Ostracod clasts testify to Pannonian origin but because they are of their being fragmental, a closer identification is not possible.

There are some proofs of reworking, as follows:

a) The stratification is different from that of the Pannonian (the basin facies of the Pannon inland lake had excellent conditions for deposition), the characteristic vertical parameter of the stratification is $10^{-1} – 10^{0}$ m: While in our case the stratification has a $10^{-3} – 10^{-2}$ m rhythmicity and on good core samples marks of cross bedding can be observed.

b) Mixing materials, characteristically coarse-grained, sandy gravel lenses showing lamellar stratification are present.

Since its material is the same as that of the Pannonian clays, it contains all the mineral and chemical components that are characteristic of the Pannonian clay.

The main component is the FeS_2, appearing as pyrite or marcasite as crystallinized, and colloidal melnikovite or hydrotroilite ($FeS_{1-2}x \cdot nH_2O$) in its hardly crystalline form. The FeS_2 is not stable under oxidizational circumstances; when becoming oxidized, it forms ferri-oxi-hydroxid and sulphuric acid.

A by-effect of the sulphate is given by the transformation of clay minerals. It is well-known from literature that in acidic environment (e.g. terrestrial weathering, acidic hydrothermal solution) kaolinite forms, and in alkaline environment (e. g. alkaline hydrothermal, marine halmirolitic decomposition) montmorillonite comes to existence. In permanently acidic environment this montmorillonite partially changes into kaolinite. This is what has happened in our case as well. Due to sulphuric acid the Pannonian clay, qualified to be halmirolitic (mainly montmorillonite and illite with less epygene kaolinite), transformed and the amount of kaolinite increased at the cost of the montmorillonite, whereas the amount of illite did not change. Thus the ion exchange capacity of the underlying bed grew less, approximately 27.4 mekv/loo g, While that of the primary Pannonian clay is 40 – 60 mekv/loo g.

The water bearing rock is a mixture of gravel and sand of various grain size where the clay fraction of the suspended load of the original sedimentary pool is also present.

The sandy gravel consists mainly of metamoprhic quartzite. Under different ground water chemical conditions only the surface coating of the quartzite emphasizes its importance. On a higher relief the congelational crust (see: congelational phenomenon) is characteristic, the limonite (FeO(OH)) and the pyrolusite (MnO_2) form a chemosorbtional surface.

The oxidizationally precipitated ferri-oxi hydroxid films are mainly in colloidal phase, the hardly mineralize at all, so they are inclined to be reversible and dissolve for reductional effects (usually as ferrohydrogene carbonates). Manganese does not form oxidizational files, the actual redox potential in the bank filtration well is smaller (+150 – +450 V) than the reduced normal redox potential of the manganese. The amount of the ferri-oxi-hydroxid coating depends on the extent of the coating; the bigger the specific surface – that is, the smaller then grain size – is, the bigger its extension will be. This is the primary role of the grain size distribution that influences the chemical properties of the water.

The most important chemical factor of the aquifer is the silt fraction. According to engineering-geological practice, it was separated by means of a sieve of 20 μm meshes (Fritsch Afnor NFX 11 – 501. No 14 standard sieve) by rinsing. We took also the 20 – 50 μm fraction under investigation in case it prooved to be active in a way.

The silt content of the sandy gravel can be of different origin. In the vicinity of the present river channel, recent kolmatation and in the vicinity of the fossil one fossil kolmatation can be observed.

The more or less equally distributed silt content of the aquifer is syngenetic and originates from the sedimentary pool of the gravelly sand, that is, from the suspended of the fossil stream.

This seems to contradict the law of sedimentation according to which the different fractions should separate (apart from silt, also gravel and sand).

However, according to our experiments this cannot be corroborated neither in the case of recent, nor in the case of fossil sediments. Probably this is covered by the dinamics of slurry movement.

The ion exchange capacity of the clay mineral can be estimated to be around the average, it cannot be measured precisely because it can hardly be separated from the components of the other fractions and even in the case of solid organic matters some surface activity, adsorbtion can be observed.

According to the X-ray analysis the composition of the clay minerals is varied, bot it is usually, on an average, of 50% montmorillonite, 20% kaolinite and 30% illite.

The organophilia of the montmorillonite cannot be measured since it cannot be separated by means of the available methods. Therefore our working hypothesis in the following was that the clay mineral and the detritus form separate adsorbtional systems (otherwise the two systems would adsorb each other thus disabling the adsorbtional capacity). Indirect measurements have made this working hypothesis plausible.

The surface activity of the suspended load has two effects: it helps some chemical processes (mainly reduction) and accumulates the transformed matters on its surface making bacterial functions possible at the same time.

The reason for this latter case can be found in the environmental conditions, for the optimal life functions of these bacteria do not meet the actual environmental conditions and bacteria can only make permanent

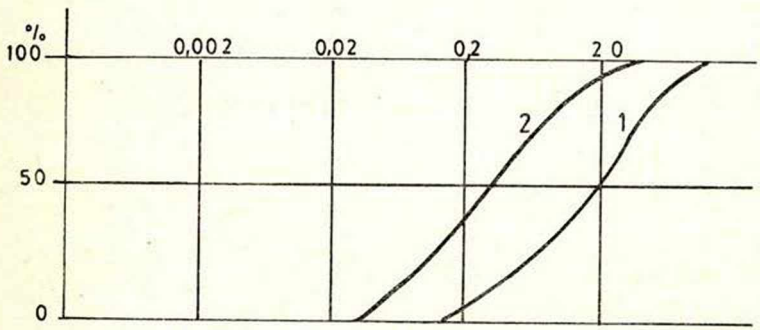

Fig. 3. Granulometry in G-1. producing well

1. 1,9 - 19,3 m gravelly sand
2. 19,3 - 22,0 m sand

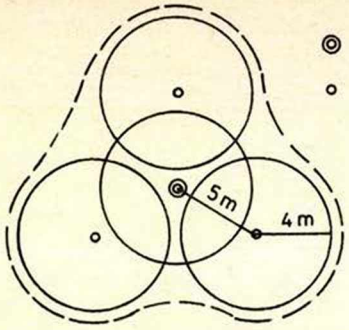

Fig. 4. Plan of oxidation zone

◎ producing well
o drain wells
(dashed) extension of oxidation zone

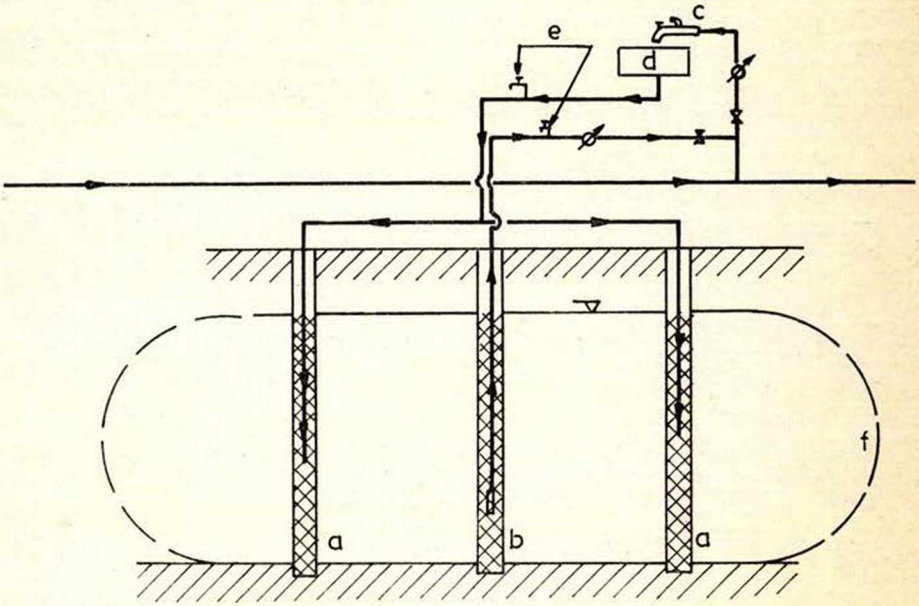

Fig. 5. Functional plan of experimental method

a. drain well
b. producing well
c. oxygenator
d. degasing unit
e. sampler valves
f. oxidation zone

microconditions (pH, Eh) in muddy rocks, where due to the bad fluid permeability, the small speed of current and diffusion does not let the two different chemical environments to mix.

The hydraulical parameters of the aquifer were determined partly upon examination of rock samples taken from boreholes and partly upon data by test pumping (see Fig. 3.).

The porosity of the gravel sand at a depth of 1,9 – 19,3 m is 10,4 – 15,7 %, its transmissivity is on an average 7.10^{-4} m/sec, the porosity at a depth of 19,3 – 22,0 m is 8,5 – 13,2%, the transmissivity is $2{,}9.10^{-5}$ sec. The resultant transmissivity as counted from the data obtained by pumping test is $3{,}6 \cdot 10^{-4}$ m/sec.

Planning the in situ iron-manganese elimination process in Vyredox system

Three absorbing wells were installed around the test well G – 1, at a distance of five metres and at an angle of 120° from it (Fig. 4.).

Counting with a porosity of 10% the pore volume of the oxidizational zone, considered to be 4 metres in radius, is 5.026 m^3/lm. Counting with an active filter length of 20 meters that is approximately 100 m^3/well, and taking the environment of the three wells and the space between them also into consideration it is 350 – 400 m^3. The diagram of function can be seen in Fig. 5.

By means of bacteria the water, enriched in oxygen oxidizes the iron and manganese thus becoming solid, according to the well-known process. The aim of the experiments was to determine the optimal technical and economical parameters of the process and to predict the expectable kolmatation of the aquifer.

Unfortunately the 9 – 11 mg/l iron content of the feed water precipitated after the oxygen enrichment and the $Fe(OH)_3$ precipitation partly kolmatated the filter of the drain-well, therefore we reorganized the system, thus solving the primary elimination of iron from the feedwater.

Three examination periods could be terminated, each lasted for three weeks. The operational conditions were the following:

– Efficiency of the oxygenator was 80 – 100%, meaning that there were approximately 9 – 11 mg/l oxygen in solution in the water at a temperatura of 10 – 12 °C;

– Enrichment took ten hours, the amount of feed-water was 400 – 500 m^3), the uplifting lasted ten hours and 500 m^3 water was obtained during the steady uplift.

The ion content of the recharged water fluctuated between 0,05 and 0,3 mg/l, its manganese content was about 1,2 – 2,1 mg/l (manganese could not be eliminated by means of airing, applied previously for iron elimination), the aggressive CO_2 content was 0,0 – 6,5 mg/l, the O_2 in solution was 8,3 – 11,0 mg/l in average, COD was 0,6 – 1,8 mg/l, the pH was 7,4 – 7,7.

The quality of the uplifted water can be seen in Figs. 6 and 7.

Though the decrease of the iron and manganese content shows a positive tendency, its value is high above the permissible limit, therefore it would have been reasonable to continue the examinations, however, due to kolmatation at the beginning of the experiment it was made impossible.

Apart from this technical failure we judge the Vyredox method to be applicable to an economical and reliable in situ iron – manganese elimination in the given hydrogeological situation.

Planning the in situ iron – manganese elimination process in Subterra system

After the kolmatation of the absorbing wells the producing well had to be operated in an alternative operational mode; that means ten hours of recharge, four hours reaction time and ten hours producing in three-week cycles.

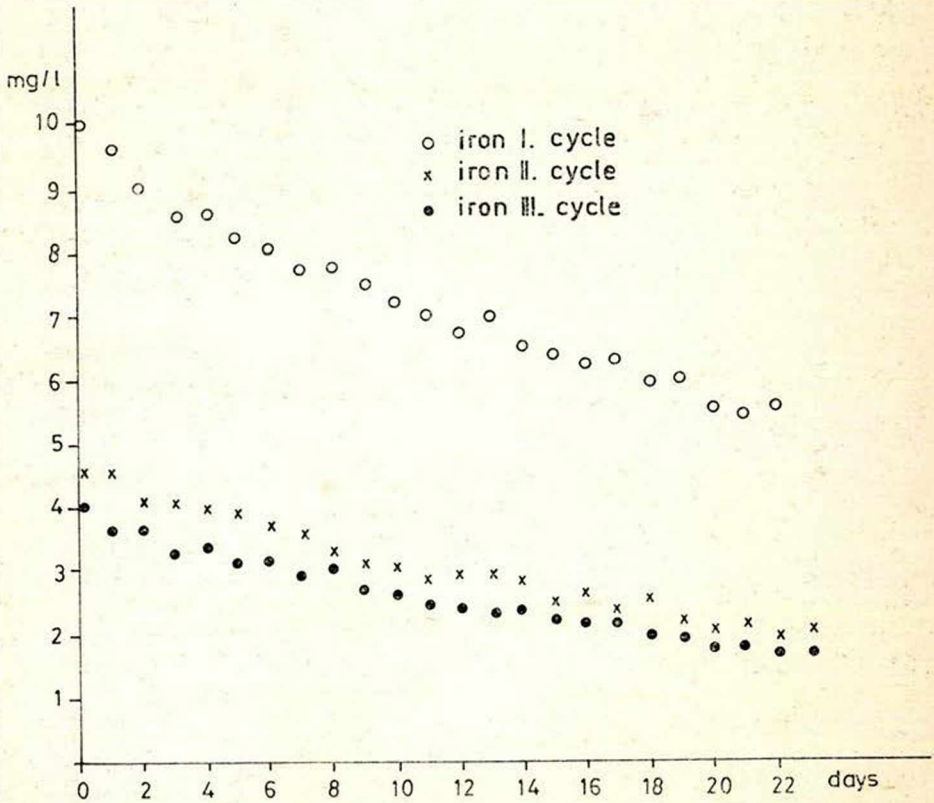

Fig.6. Change of iron concentration in produced water (Vyredox-method)

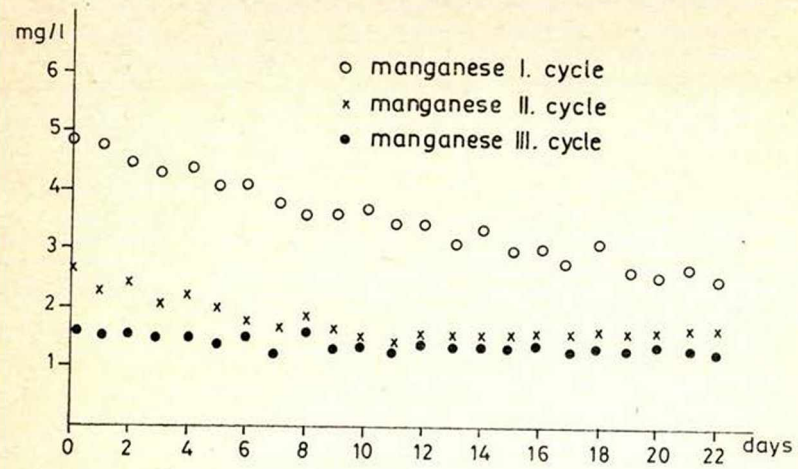

Fig. 7. Change of manganese concentration in produced water (Vyredox - method)

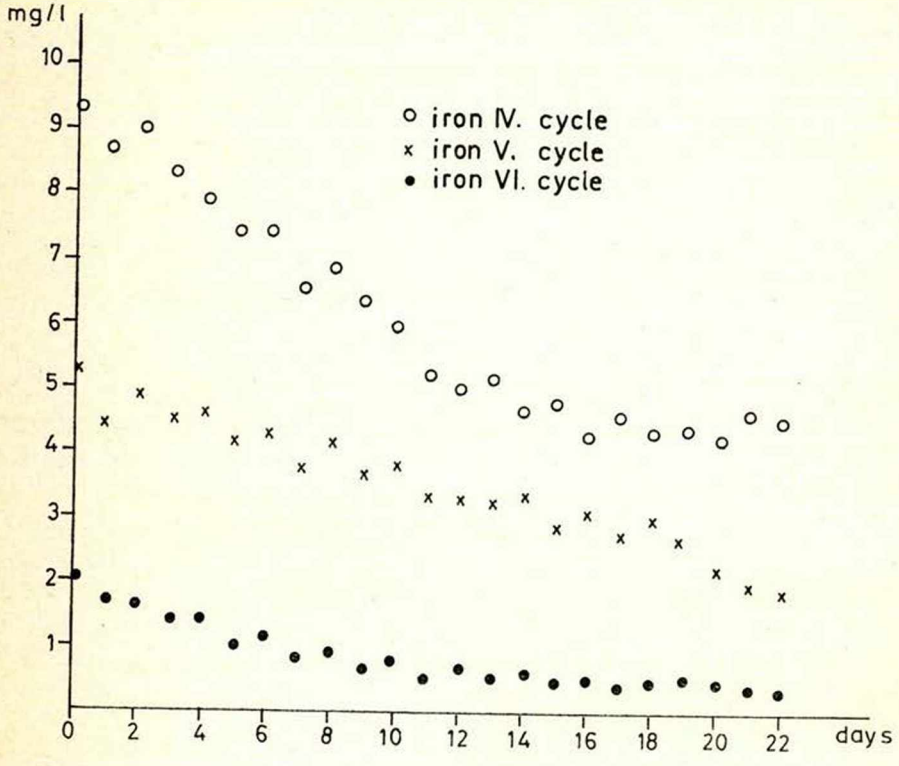

Fig. 8. Change of iron concentration in produced water (SUBTERRA - METHOD)

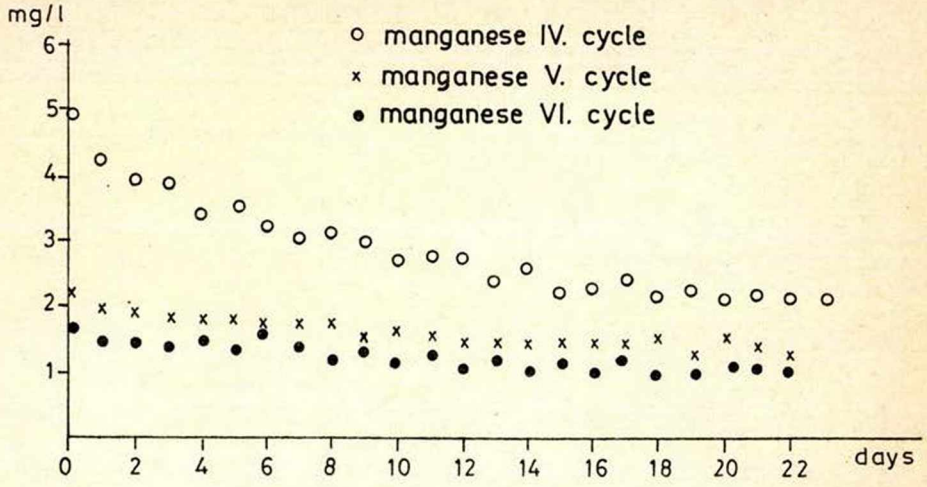

Fig. 9. Change of manganese concentration in produced water (Subterra – method)

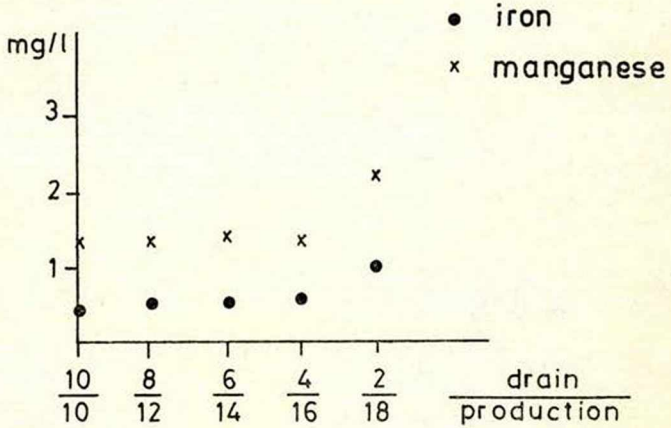

Fig. 10. Change of iron and manganese concentration as a function of rate drain/production

We mention that the consequence of the previous Subterra experiment (adsorbtional catalythic and chemosorbtional coating on the rock grains) were stopped by a one-year production thus the Subterra cycle started according to the original condition.

The quality of the recharged water was the same and at the preliminary surface iron elimination the concentration of the manganese did not decrease.

Experiences at other waterworks confirmed that if we employ more wells alternatively the increasing quality of the produced water will also mean the increasing quality of the recharged water which leads to a self-improving process.

The decrease of the iron and manganese content of the produced water is shown in Figs. 8 and 9. By the end of the sixth cycle, that is, after 60 days the iron content decreased permanently to 0,5 mg/l which can be considered to be a satisfactory result, but, due to the high manganese content of the recharged water the manganese did not decrease to the desired level.

The cycles IV – V – VI. proved the utility of the Subterra method under the given hydrogeological conditions. Further examinations were needed to decide the economical operational time ratio, that is, the proportion of the phases in a 24-hour-period had to be varied.

Since the maximum intensity of both the recharge and the producing was fixed by the small ($K = 3{,}6 \cdot 10^{-4}$ m/sec) transmissivity, the problem was solved by the change of the time ratio. Leaving the four hours reaction time unchanged the ratio of recharging and producing changed as seen below:

recharging	producing
10 hours	10 hours
8 hours	12 hours
6 hours	14 hours
4 hours	16 hours
2 hours	18 hours

It can be seen in Fig. 10, that there is no significant change in the concentration at the end of a period till the ratio is 4:6, but then the values increase abruptly to ratio of 2:18.

This coincides with our experiences that in aquifers where the grain-size frequency distribution is badly sorted, the in situ iron and manganese elimination, due to the small pore size, is on the bounds of economic rentability.

REFERENCES

FILLIS, J. – MOLOF, A. H. (1972): Effect of benthal deposits on oxygen and nutrient economy of flowing waters – J. WPCF 44. 4 pp. 644 – 62.

FLICK, G. (1968): Versuche zur Entmanganung eines Wassers auf adsorptiv-katalytischem Entmanganungsmaterial Neue Deliwa Zeitschrift H. 3.

GONDOS, GY. (1970): Relationship between the dissolved iron and manganese compounds in water and the mineralogical composition of the aquifer 2nd Conference on Water Quality and Technology Budapest.

HÄSSELBARTH, U. – LÜDEMANN, D. (1967): Die biologische Verockerung von Brunnen durch Massenentwicklung von Eisen und Manganbakterien. Bohrtechnik – Brunnenbau – Rohrleitungsbau, Berlin 10 – 11. sz.

ROTT, U. – BOOCHS, P. W. – BAROVIC, G. (1978): Unterirdische Grundwasser-aufbereitung durch Einleitung von sauerstoffhaltigem Wasser in den Boden – Wasser und Boden 8.

SEYFRIED, C. F. – ROTT, U. (1975): Verfahren zur Reinigung von Grundwasser von Mangan oder anderen löslichen Substanzen im Untergrund. BDPa.

SEYFRIED, C. F. – ROTT, U. (1977): Grenzen und Möglichkeiten der subterrestrischen Wasseraufbereitung. Mitteilung der Subterra Methoden.